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<table style="width: 100%; border: none;"> <tr> <td style="width: 45%; vertical-align: top; padding: 5px;"> <p>(21) International Application Number: PCT/US96/05160</p> <p>(22) International Filing Date: 15 April 1996 (15.04.96)</p> <p>(30) Priority Data: 08/436,141 8 May 1995 (08.05.95) US</p> <p>(60) Parent Application or Grant (63) Related by Continuation US 08/436,141 (CON) Filed on 8 May 1995 (08.05.95)</p> <p>(71) Applicant (for all designated States except US): CREE RESEARCH, INC. [US/US]; Suite 176, 2810 Meridian Parkway, Dusham, NC 27713 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): EDMOND, John, Adam [US/US]; 206 W. Jules Verne Way, Cary, NC 27511 (US). KONG, Hua-Shuang [CN/US]; 10840 Bexhill Drive, Raleigh, NC 27606 (US).</p> <p>(74) Agents: SUMMA, Philip et al.; Bell, Seltzer, Park &amp; Gibson, P.O. Drawer 34009, Charlotte, NC 28234 (US).</p> </td> <td style="width: 55%; vertical-align: top; padding: 5px;"> <p>(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> With international search report.</p> </td> </tr> </table>			<p>(21) International Application Number: PCT/US96/05160</p> <p>(22) International Filing Date: 15 April 1996 (15.04.96)</p> <p>(30) Priority Data: 08/436,141 8 May 1995 (08.05.95) US</p> <p>(60) Parent Application or Grant (63) Related by Continuation US 08/436,141 (CON) Filed on 8 May 1995 (08.05.95)</p> <p>(71) Applicant (for all designated States except US): CREE RESEARCH, INC. [US/US]; Suite 176, 2810 Meridian Parkway, Dusham, NC 27713 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): EDMOND, John, Adam [US/US]; 206 W. Jules Verne Way, Cary, NC 27511 (US). KONG, Hua-Shuang [CN/US]; 10840 Bexhill Drive, Raleigh, NC 27606 (US).</p> <p>(74) Agents: SUMMA, Philip et al.; Bell, Seltzer, Park &amp; Gibson, P.O. Drawer 34009, Charlotte, NC 28234 (US).</p>	<p>(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> With international search report.</p>
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<p>(54) Title: DOUBLE HETEROJUNCTION LIGHT EMITTING DIODE WITH GALLIUM NITRIDE ACTIVE LAYER</p>				
<p>(57) Abstract</p> <p>A double heterostructure (24) for a light emitting diode (20) comprises a layer of aluminum gallium nitride a first conductivity type (25); a layer of aluminum gallium nitride having the opposite conductivity type (27); and an active layer of gallium nitride (26) between the aluminum gallium nitride layers, in which the gallium nitride layer is co-doped with both a Group II acceptor and a Group IV donor, with one of the dopants being present in an amount sufficient to give the gallium nitride layer a net conductivity type, so that the active layer forms a p-n junction with the adjacent layer of aluminum gallium nitride having the opposite conductivity type.</p>				

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DOUBLE HETEROJUNCTION LIGHT EMITTING  
DIODE WITH GALLIUM NITRIDE ACTIVE LAYER

Field of the Invention

The present invention relates to light emitting diodes, and in particular, relates to light emitting diodes formed in semiconductor materials with  
5 sufficiently wide band gaps to emit light in the blue portion of the visible spectrum.

Background of the Invention

A light emitting diode ("LED") is a photonic semiconductor device. Photonic semiconductor devices  
10 fall into three categories: devices that convert electrical energy into optical radiation (LED's and diode lasers), devices that detect optical signals (photodetectors), and devices that convert optical radiation into electrical energy (photovoltaic devices  
15 or solar cells).

Although all three of these categories or devices have useful applications, the LED may be the most commonly recognized because of its application to such a wide variety of products and applications such  
20 as scientific equipment, medical equipment, and perhaps most commonly, various consumer products in which LEDs form the light source for various signals, indicators, gauges, clocks, and many other familiar items.

Semiconductor sources such as LEDs are  
25 particularly desirable as light output devices in such items because of their generally long lifetime, their low power requirements, and their high reliability.

In spite of their widespread use, LEDs are to some extent functionally limited, because the color  
30 that an LED can produce is fundamentally limited by the nature of semiconductor materials in which the LED is formed. As well known to those of ordinary skill in

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this and related arts, the light produced by an LED is referred to as "electroluminescence" and represents the generation of light by an electric current passing through a material under an applied electric field.

5 Any given material that produces electroluminescent light tends to do so over a relatively narrow range of wavelengths under given circumstances. Electroluminescence thus differs from thermal radiation or incandescence which generally have much broader  
10 spectral widths.

More fundamentally, an LED's luminescence is produced by basic quantum mechanical transitions between energy levels within the semiconductor material. Because the bands within a material depend  
15 both upon the material and its doping, the energy of the transition, and thus the color of the radiation it produces, is limited by the well known relationship ( $E=h\nu$ ) between the energy ( $E$ ) of a transition and the frequency ( $\nu$ ) of the light it produces ( $h$  is Plank's  
20 constant). Blue light has a shorter wavelength (and thus a higher frequency) than the other colors in the visible spectrum, and thus must be produced from transitions that are greater in energy than those transitions which produce green, yellow, orange or red  
25 light.

More specifically, the entire visible spectrum runs from the violet at about 390 nanometers to the red at about 770 nanometers. In turn, the blue portion of the visible spectrum can be considered  
30 (somewhat arbitrarily) to extend between the wavelengths of about 425 and 480 nanometers. The wavelengths of 425 and 480 nanometers in turn represent energy transitions (also somewhat arbitrarily) of about 2.6 eV and about 2.9 eV. Accordingly, only materials  
35 with a bandgap of at least about 2.6 eV can produce blue light, even under the best of conditions.

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As is further well recognized, blue is one of the primary colors, and thus any devices which hope to produce full color displays using LEDs need to incorporate blue in some fashion. Absent efficient  
5 blue LEDs, some other method such as filtering or shuttering must be used to produce a blue contribution to a display that otherwise lacks a blue LED source.

From another standpoint, blue light's shorter wavelength allows it to be used to store more  
10 information on optical memory devices (such as CD ROM) than can red or yellow light. In particular, a CD ROM of a given physical size can hold about eight times as much information using blue light than it could when using red light. Thus, the advantages for computer and  
15 other sorts of optical memories using blue light are quite attractive.

Candidate materials with sufficient bandgaps to produce blue light include silicon carbide, gallium nitride, other Group III nitrides, zinc sulfide, and  
20 zinc selenide. More common semiconductor materials such as silicon, gallium phosphide, or gallium arsenide are unsuitable for producing blue light because their bandgaps are on the order of 2.26 eV or less.

The last decade has seen a great deal of  
25 progress in both the basic and commercial development of blue light emitting diodes, including a number of contributions by the assignee of the present invention. These include U.S. Patents No. 4,918,497; 4,966,862; 5,027,168; and 5,338,944.

30 Another candidate material for blue light emitting diodes is gallium nitride (GaN) and its analogous Group III (i.e. Group III of the periodic table) nitride compounds such as aluminum gallium nitride (AlGaN), indium gallium nitride (InGaN), indium  
35 aluminum nitride (InAlN) and in some circumstances indium aluminum gallium nitride (InAlGaN). These materials are particularly attractive because they

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offer direct energy transitions with bandgaps from between about 3.4 to about 6.2 eV at room temperature. As known to those familiar with LEDs and electronic transitions, a direct (or "vertical") transition occurs  
5 in a semiconductor when the valence band maxima and the conduction band minima have the same K value, which in turn means that crystal momentum is conserved during the transition so that the energy produced by the transition can go predominantly into the photon; i.e.  
10 to produce light rather than heat. When the conduction and valence band minima are not of the same K value, a phonon (i.e. an emission of vibrational energy) is required to conserve crystal momentum and the transition is called "indirect." The phonon's energy  
15 essentially reduces the energy of any resulting photon, thus reducing both the frequency and the intensity of the emitted light. A full discussion of the theory and operation of LEDs is given in Chapter 12 of Sze, Physics of Semiconductor Devices, Second Edition  
20 (1981), pp. 681ff.

From a more lay point of view, the direct transition characteristics of group III nitrides, including gallium nitride, offer the potential for brighter and more efficient emissions--and thus  
25 brighter and more efficient LEDs--than do the emissions from indirect materials such as silicon carbide, all other factors being generally equal.

Accordingly, much interest in the last decade has also focused on producing light emitting diodes in  
30 gallium nitride and the related group III nitrides.

Although gallium nitride offers a direct transition over a wide bandgap, and thus a theoretically greater brightness, the material presents a particular set of technical problems in manufacturing  
35 working devices. The primary problem is the lack of bulk single crystals of gallium nitride which in turn means that gallium nitride or other group III nitride

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devices must be formed as epitaxial layers on other materials. The most commonly used material to date has been sapphire (aluminum oxide,  $\text{Al}_2\text{O}_3$ ). Sapphire offers a reasonable crystal lattice match to Group III

5 nitrides, thermal stability, and transparency, all of which are generally useful in producing a light emitting diode. Sapphire offers the disadvantage, however, of being unsuitable for conductivity doping. In turn, this means that the electric current that must

10 be passed through an LED to generate the emission cannot be directed through the sapphire substrate. Thus other types of connections to the LED must be made. In general, LEDs with "vertical" geometry (i.e. using conductive substrates so that ohmic contacts can

15 be placed at opposite ends of the device) are preferred for a number of reasons, including their easier manufacture than such "nonvertical" devices.

Accordingly, the assignee of the present invention has developed the use of silicon carbide

20 substrates for gallium nitride and other Group III devices as a means of solving the conductivity problems of sapphire as a substrate. Because silicon carbide can be doped conductively, "vertical" LEDs can be formed on it; i.e. devices in which one contact can be

25 made to the top of a device and the second contact to the bottom of the device, a structure which greatly facilitates the manufacture of the LED as well as the incorporation of the LED into circuits or combination devices or structures.

30 In spite of these theoretical advantages, a consistently reliable and predictable blue emission using a gallium nitride active layer has yet to be accomplished. For example, some workers have used silicon and zinc to co-dope or compensate indium

35 gallium nitride ( $\text{InGaN}$ ) but have interpreted their results to mean that gallium nitride standing alone is not suited as well as  $\text{InGaN}$  for an LED because  $\text{InGaN}$

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gives a better band-to-band ("interband") transition for a light emitting diode.

Similarly, others have prepared heterojunctions from AlGa<sub>N</sub> and Ga<sub>N</sub>, but never attempted  
5 or described compensated doping, and by all indications, used an intrinsic n-type gallium nitride and p-type AlGa<sub>N</sub> for the junction. Indeed, if some of the prior art structures are properly understood, doping them with a compensating acceptor such as zinc  
10 would have produced an insulating layer rather than a compensated one.

#### Object and Summary of the Invention

Accordingly, it is an object of the present invention to provide a light emitting diode that takes  
15 advantage of gallium nitride's properties, that does so to produce an emission that is both consistent and predictable, and that does so using a compensated active layer.

The invention meets this object with a double  
20 heterostructure for a light emitting diode, said heterostructure comprising a layer of aluminum gallium nitride having a first conductivity type; a layer of aluminum gallium nitride having the opposite conductivity type; and a conductive layer of gallium  
25 nitride between said aluminum gallium nitride layers, said gallium nitride layer being co-doped with both a Group II acceptor and a Group IV donor, with one of said dopants being present in an amount sufficient to give said gallium nitride layer a net conductivity  
30 type, and forming a p-n junction with the adjacent layer of aluminum gallium nitride having the opposite conductivity type therefrom.

In another aspect the invention comprises a double heterostructure light emitting diode that emits  
35 in the blue portion of the visible spectrum and comprising a substrate;



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a buffer layer on said substrate; and the double heterostructure of the invention on the buffer layer.

In yet a third aspect, the invention comprises a method of producing an active layer of  
5 compensated n-type gallium nitride for a double heterostructure light emitting diode that emits in the blue portion of the visible spectrum

The foregoing and other objects, advantages and features of the invention, and the manner in which  
10 the same are accomplished, will become more readily apparent upon consideration of the following detailed description of the invention taken in conjunction with the accompanying drawings, which illustrate preferred and exemplary embodiments, and wherein:

15        Brief Description of the Drawings

Figure 1 is a cross-sectional view of a first embodiment of a light-emitting diode (LED) according to the present invention;

Figure 2 is a cross-sectional view of a  
20 second embodiment of an LED according to the present invention;

Figure 3 is a scanning electron micrograph of an LED manufactured according to the present invention;

Figure 4 is a plot of spectral output versus  
25 current for an LED according to the present invention;

Figure 5 is a plot of output and efficiency versus forward current for an LED according to the present invention;

Figure 6 is a plot of the normalized  
30 photoluminescence intensity versus wavelength for aluminum gallium nitride ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ );

Figure 7 is a plot of current versus voltage for ohmic contacts made to n-type gallium nitride on silicon carbide;

35        Figure 8 is a plot similar to Figure 7 except with the ohmic contact made to p-type gallium nitride;

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Figure 9 is a plot of the current-voltage characteristics of an LED according to the present invention;

Figure 10 is a plot of the room temperature photoluminescence of magnesium doped p-type gallium nitride on silicon carbide;

Figure 11 is a Hall effect plot demonstrating the carrier concentration and resistivity of the n-type gallium nitride layer as a function of temperature;

Figure 12 illustrates the mobility data for a silicon doped n-type gallium nitride layer on silicon carbides;

Figure 13 is another Hall effect plot showing the hole concentration and resistivity of magnesium doped gallium nitride as a function of temperature; and

Figure 14 is a plot of the mobility data for a magnesium doped p-type gallium nitride layer on silicon carbide.

#### Detailed Description

In its broadest aspect, the invention is a double heterostructure for a light emitting diode comprises a layer of aluminum gallium nitride having a first conductivity type; a layer of aluminum gallium nitride having the opposite conductivity type; and an active layer of gallium nitride between the aluminum gallium nitride layers, in which the gallium nitride layer is co-doped with both a Group II acceptor and a Group IV donor, with one of the dopants being present in an amount sufficient to give the gallium nitride layer a net conductivity type, so that the active layer forms a p-n junction with the adjacent layer of aluminum gallium nitride having the opposite conductivity type.

In a preferred embodiment, the invention is a double heterostructure for a light emitting diode in which the heterostructure comprises a p-type layer of

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aluminum gallium nitride, an n-type layer of aluminum gallium nitride, and an n-type layer of gallium nitride between the aluminum gallium nitride layers. The gallium nitride layer is codoped with both zinc and  
5 silicon and forms a p-n junction with the p-type layer of aluminum gallium nitride.

The double heterostructure offers several advantages over homostructure or single heterostructure devices. These can include enhanced emission based on  
10 the different refractive indexes between GaN and AlGaIn; more efficient carrier confinement, which in turn leads to more efficient carrier recombination and thus a brighter output in an LED.

In a preferred embodiment, the double  
15 heterostructure will be incorporated in light emitting diode such as the one broadly designated at 20 in Figure 1. The double heterostructure light emitting diode 20 illustrated in Figure 1 emits in the blue portion of the visible spectrum and comprises a  
20 substrate 21 preferably formed of silicon carbide that has been sufficiently doped to provide a conductive substrate for the vertical structure LED 20 illustrated in Figure 1. In order to match the crystal structure of the buffer and aluminum gallium nitride layers on  
25 the substrate 21, the silicon carbide substrate has a polytype preferably selected from the group consisting of 6H or 4H silicon carbide.

As known by those familiar with these materials, 4H and 6H are two of the hexagonal crystal  
30 forms of silicon carbide, and on which gallium nitride (and other Group III nitrides) form hexagonal polytypes. If cubic (e.g. 3C) silicon carbide is used as the substrate, however, gallium nitride can also form a cubic structure.

35 The LED 20 next includes a buffer layer 22 on the substrate 21. Appropriate buffer layers are described in U.S. Patent No. 5,393,993. The buffer

structure provides an appropriate crystal and electronic transition between the silicon carbide substrate and the double heterostructure portion of the LED 20.

5           In one embodiment the buffer layer comprises a first layer of gallium nitride and aluminum nitride; and a second layer of gallium nitride and aluminum nitride adjacent to the first layer. The mole percentage of aluminum nitride in the second layer is  
10 substantially different from the mole percentage of aluminum nitride in the first layer.

          In another embodiment the buffer layer comprises a conductive layer selected from the group consisting of gallium nitride, aluminum nitride, indium  
15 nitride, ternary Group III nitrides having the formula  $A_xB_{1-x}N$ , where A and B are Group III elements and where x is zero, one, or a fraction between zero and one, quaternary Group III nitrides having the formula  $A_xB_yC_{1-x-y}N$  where A, B, and C are Group III elements; x and y,  
20 are zero, one, or a fraction between zero and one, and 1 is greater than (x + y), and alloys of silicon carbide with such ternary and quaternary Group III nitrides.

          In yet another embodiment, the buffer layer  
25 comprises a first layer upon the substrate formed of a graded composition of silicon carbide aluminum gallium nitride in which the portion adjacent the substrate is substantially entirely silicon carbide and the portion furthest from the substrate is substantially entirely  
30 aluminum gallium nitride with the portions therebetween being progressively graded in content from predominantly silicon carbide to predominantly aluminum gallium nitride. A second layer can be added to the first layer, and can be formed of a graded composition  
35 of aluminum gallium nitride.

          In preferred embodiments, the LED 20 further comprises an n-type gallium nitride epitaxial layer 23

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on the buffer layer 22 which provides an additional crystal transition between the substrate, the buffer, and the heterostructure.

The LED 20 next includes a double heterostructure indicated by the brackets 24 in Figure 1. The double heterostructure 24 includes an n-type layer of aluminum gallium nitride 25 which, when the n-type gallium nitride epitaxial layer 23 is included in the structure, rests upon the n-type gallium nitride epitaxial layer 23. The n-type layer 25 of aluminum gallium nitride has the formula  $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $x$  designates the mole fraction of aluminum, and where 1 is greater than  $x$  and  $x$  is greater than 0 ( $1 > x > 0$ ). In preferred embodiments the mole fraction  $x$  is between about 0.05 and 2.0, and in the most preferred embodiments, the mole fraction  $x$  is about 0.1. The aluminum gallium nitride layer 25 furthermore has a net doping density of about  $2\text{E}18$  and is doped with silicon in the most preferred embodiments. As commonly used in this art, "E" is an abbreviated exponential notation for dopant density, so that  $2\text{E}18$  represents  $2 \times 10^{18} \text{cm}^{-3}$ .

The double heterostructure 24 includes an active layer 26 of gallium nitride on the n-type aluminum gallium nitride layer 25 which, as noted above, is compensated with a Group II acceptor and a Group IV donor, and in which the preferred Group II acceptors are zinc or cadmium or magnesium, and in which carbon can comprise a Group IV acceptor. The preferred Group IV donor is silicon or germanium. In the most preferred embodiments, the Group II acceptor is zinc, and the Group IV donor is silicon as these produce the characteristic blue emission described herein with respect to a number of the other drawings. The net doping density of the active layer 26 is between about  $1\text{E}18$  and  $4\text{E}18$ , and most preferably about  $2\text{E}18$ .

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The double heterostructure is completed with a p-type aluminum gallium nitride layer 27 which has the formula

$\text{Al}_x\text{Ga}_{1-x}\text{N}$  where one is greater than x and x is greater  
5 than 0 ( $1 > x > 0$ ), and in which the preferred mole  
fraction x is also between about 0.05 and 2.0, and most  
preferably about 0.1.

In preferred embodiments, the LED 20 can  
further comprise a p-type gallium nitride layer 30 on  
10 the top p-type layer 27 of the heterostructure. The p-  
type layer 27 has a net doping density of about  $1\text{E}19$   
and is preferably doped with aluminum.

The LED 20 illustrated in Figure 1 further  
comprises respective ohmic contacts 31 to the substrate  
15 and 32 to the top layer; i.e. to the p-type gallium  
nitride layer 30 in the embodiment illustrated in  
Figure 1. It will be understood, however, that in  
embodiments that do not include the p-type gallium  
nitride layer 30, the ohmic layer 32 is made directly  
20 to the p-type aluminum gallium nitride layer 27 of the  
double heterostructure.

Figure 1 also illustrates that in preferred  
embodiments, the contact 32 comprises a bonding pad of  
titanium and gold. In a most preferred embodiment, the  
25 contact is formed from a thin layer of titanium (Ti)  
overlaid with a layer of gold (Au). In a preferred  
embodiment, the basic contact 32 is accompanied by a  
transparent ohmic contact 33 which extends across a  
larger portion of the top surface of the LED 20 to help  
30 spread current and thus increase brightness.

A preferred ohmic contact to the silicon  
carbide substrate comprises nickel, but can also  
comprise other appropriate metals or metal combinations  
such as nickel-vanadium.

35 The double heterostructure light emitting  
diode 20 illustrated in Figure 1 will consistently  
produce an emission with a peak wavelength of about 430

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nanometers (nm) and a bandwidth at half maximum of about 65 nm when a typical LED current (for example between 10 and 40 milliamps) is applied across the p-n junction that is formed by the aluminum gallium nitride layer 27 of the heterostructure and the gallium nitride active layer 26 of the heterostructure 24.

Figure 2 shows a slightly different embodiment of an LED 40 according to the present invention. In Figure 2, the substrate is shown at 41, and the buffer layer is shown at 42, but which in this embodiment comprises an insulating buffer layer. As noted earlier herein, the buffer layer can comprise the structure disclosed in U.S. Patent No. 5,393,993. Alternatively, the buffer layer 42 can comprise a graded layer of AlGaN that is substantially entirely aluminum nitride where it meets the substrate 41, and then is progressively graded with increasing amounts of gallium until it is substantially entirely gallium nitride at its upper surface where it meets the n-type layer of gallium nitride shown as 43 in Figure 2 and as 23 in Figure 1.

The double heterostructure is illustrated at 44 in Figure 2 and in a preferred embodiment comprises the n-type aluminum gallium nitride layer 45 that otherwise corresponds to the layer 25 described with respect to Figure 1, a compensated n-type gallium nitride active layer 46 which likewise corresponds to the gallium nitride active layer 26 described with respect to Figure 1, and a p-type aluminum gallium nitride layer 47 which similarly corresponds to the layer 27 described with respect to Figure 1. A p-type gallium nitride layer 50 corresponding to layer 30 in Figure 1 is on the heterostructure, and the ohmic contacts 51 to the substrate and 52 and 53 to the top of the diode correspond to those described as 31, 32, and 33 in Figure 1.

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As Figure 2 illustrates, however, because the buffer layer 42 in this embodiment is insulating rather than conductive, some other path for current flow must be provided between the ohmic contact 51 on the substrate and the ohmic contacts 52 and 53 on the top layer of the diode. This contact is made through shorting contacts 54 and 55 which are preferably formed on aluminum or titanium and aluminum and which provide an ohmic contact to the n-type gallium nitride layer 43. In the most preferred embodiments, these shorting contacts further include portions illustrated at 56 and 57 that are in immediate contact with the n-type silicon carbide substrate and which are formed of titanium and nickel to produce an appropriate ohmic contact with the silicon carbide.

In another aspect, the invention comprises a method of producing an active layer of compensated gallium nitride for a double heterostructure light emitting diode that emits in the blue portion of the visible spectrum. In this aspect, the invention comprises introducing vaporized sources of gallium, nitrogen, silicon and zinc into a chemical vapor deposition system that includes a semiconductor substrate compatible with the growth of gallium nitride thereon. The temperature is maintained high enough to promote the epitaxial growth of zinc and silicon compensated gallium nitride, but lower than the temperature at which the gallium nitride would decompose. As is well understood by those of ordinary skill in this art, the temperature must be high enough to provide the energy required to get atoms to move across the epitaxial growth surface, and in preferred embodiments of the present invention, this temperature is generally maintained between about 800°C and 1050°C.

It will be further understood by those of ordinary skill in this art, that gas flow rates and specific temperatures are generally system-dependent,



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and thus specific temperatures and the like other than those recited herein will fall within the method aspects of the invention because they can be easily determined for particular chemical vapor deposition ("CVD") systems by those of ordinary skill in this art and without undue experimentation.

As another limiting factor, the temperature is preferably maintained lower than the temperature at which the surface morphology of the epitaxial layer would become unacceptable for further epitaxial growth thereon.

In preferred embodiments, the step of introducing the vaporized source of gallium comprises introducing trimethyl gallium,  $(\text{CH}_3)_3\text{Ga}$ ; the step of introducing a vaporized source of nitrogen comprises introduces ammonia,  $\text{NH}_3$ ; the step of introducing a vaporized source of zinc comprises introducing dimethyl zinc,  $(\text{C}_2\text{H}_5)_2\text{Zn}$ ; and the step of introducing a vaporized source of silicon comprises introducing silane,  $\text{SiH}_4$ . The preferred aluminum source (for the AlGaIn layers) is trimethyl aluminum,  $(\text{CH}_3)_3\text{Al}$ ; and when magnesium is introduced, the preferred source is biscyclopentadienyl magnesium,  $(\text{C}_5\text{H}_5)_2\text{Mg}$ .

Figure 3 is an SEM photograph of an LED according to the present invention. Such a device has a chip size of about 14 mil x 14 mil, with a 10 mil x 10 mil mesa portion. The substrate is about 7 or 8 mils thick, the n-GaN layer (e.g. 23 in Figure 1 or 43 in Figure 2) is about 3 microns thick and the layers in the heterostructure (n-AlGaIn, GaN, and p-AlGaIn ) are each about 1000 angstroms ( $\text{\AA}$ ) thick. The top GaN layer (e.g. 30 in Figure 1 and 50 in Figure 2) is about 4000 $\text{\AA}$  thick.

Figures 4-14 illustrate various performance characteristics of the layers that make up the heterostructure and heterostructure diode according to the present invention. Figure 4 illustrates the

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spectral response of a gallium nitride double heterojunction light emitting diode formed on a silicon carbide substrate according to the present invention as a function of operating current. Figure 4 shows  
5 measurements made at four different currents between 10 and 40 milliamps (mA). The peak emission wavelength is 430 nanometers (nm) with a bandwidth at half maximum of about 60 nanometers which is characteristic of the silicon and zinc compensated gallium nitride active  
10 layer.

Figure 5 illustrates the power output and external quantum efficiency of a light emitting diode according to the present invention as a function of operating current. As a normal operating current for  
15 such an LED (i.e. approximately 20 milliamps), the output is approximately 850 microwatts which corresponds to an external quantum efficiency of about 1.5%.

Figure 6 illustrates the room temperature  
20 photoluminescence of various combinations of aluminum gallium nitride on silicon carbide substrates and also including a pure gallium nitride layer for comparative purposes. The clean, well defined peaks that are measured at room temperature demonstrate the high  
25 crystal quality of these layers. These photoluminescent measurements were made by exciting the layers with a 10 milliwatt helium/cadmium laser at 325 nanometers.

Figure 7 demonstrates the current voltage  
30 characteristics of ohmic contacts made to n-type gallium nitride on silicon carbide substrates according to the present invention. The preferred ohmic contact metal is aluminum which yields a contact resistance of about  $10^{-5}$  ohm-cm<sup>2</sup> for an n-type gallium nitride layer  
35 with a donor density of about  $10^{18}$  cm<sup>-3</sup>.

Figure 8 is a similar current voltage plot demonstrating the characteristics of ohmic contacts

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made to p-type gallium nitride on silicon carbide substrates according to the present invention. The preferred ohmic contact metal is an alloy of titanium and gold which yields a contact resistance of approximately  $10^{-2}$  ohms-cm<sup>2</sup> for a p-type acceptor density of approximately  $6E17$  in the gallium nitride layer.

Figure 9 is the current voltage (I-V) curve for a gallium nitride double heterojunction light emitting diode on silicon carbide according to the present invention. In reverse bias no leakage current is detected. Under forward bias the LED begins to turn on at about 2.7 volts and exhibits an operating voltage of about 3.7 volts at a typical current of 20 milliamps.

Figure 10 illustrates the room temperature photoluminescence of magnesium doped p-type gallium nitride on silicon carbide. The peak occurs at about 435 nanometers for a layered doped to a net acceptor concentration of about  $6E17$ .

Figure 11 is a partial logarithmic plot of Hall effect data showing the carrier concentration and resistivity of an n-type gallium nitride as a function of temperature, plotted inversely to temperature. The layer from which the measurements for Figure 11 were taken was doped with silicon to a net donor concentration of about  $1.4E18$  and had a resistivity of 0.016 ohm-centimeter at room temperature.

Figure 12 is corresponding data for the same layer as illustrated by Figure 11, but demonstrating mobility for the layer. The mobility of the layer is approximately 300 cm<sup>2</sup>/V•s at room temperature, a high value for this doping level indicating the high quality nature of the layer.

Figure 13 is a plot of Hall effect data showing the acceptor concentration and resistivity of magnesium doped gallium nitride as a function of

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temperature (plotted inversely). The net acceptor concentration for this layer was about  $6E17$  and showed a resistivity of about 1.3 ohms-centimeter at room temperature.

5                   Figure 14 illustrates the corresponding mobility data for the same layer as Figure 13 and illustrates that the mobility of the layer is approximately  $8 \text{ cm}^2/\text{V}\cdot\text{s}$  at room temperature which is typical of the mobility of p-type gallium nitride.

10                   In the drawings and specification, there have been disclosed typical preferred embodiments of the invention and, although specific terms have been employed, they have been used in a generic and descriptive sense only and not for purposes of  
15 limitation, the scope of the invention being set forth in the following claims.

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## THAT WHICH IS CLAIMED:

1. A double heterostructure for a light emitting diode, said heterostructure comprising:

a layer of aluminum gallium nitride having a first conductivity type;

5 a layer of aluminum gallium nitride having the opposite conductivity type; and

an active layer of gallium nitride between said aluminum gallium nitride layers, said gallium nitride layer being co-doped with both a Group II  
10 acceptor and a Group IV donor, with one of said dopants being present in an amount sufficient to give said gallium nitride active layer a net conductivity type, said active layer forming a p-n junction with the adjacent layer of aluminum gallium nitride having the  
15 opposite conductivity type therefrom.

2. A double heterostructure according to Claim 1 wherein said gallium nitride layer is n-type, said Group II acceptor is zinc, and said Group IV donor is silicon.

20 3. A double heterostructure for a light emitting diode, said heterostructure comprising:  
a p-type layer of aluminum gallium nitride;  
an n-type layer of aluminum gallium nitride;  
and

25 an n-type layer of gallium nitride between said aluminum gallium nitride layers, said gallium nitride layer being co-doped with both zinc and silicon and forming a p-n junction with said p-type layer of aluminum gallium nitride.

30 4. A double heterostructure light emitting diode that emits in the blue portion of the visible spectrum and comprising:  
a substrate;

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a buffer layer on said substrate; and  
a double heterostructure on said buffer  
layer, said double heterostructure comprising:

5 an n-type layer of aluminum gallium  
nitride;

a compensated n-type active layer of  
gallium nitride on said n-type aluminum  
gallium nitride layer; and

10 a p-type layer of aluminum gallium  
nitride on said gallium nitride layer, said  
p-type layer of aluminum gallium nitride and  
said n-type active layer forming a p-n  
junction.

5. A double heterostructure light emitting  
15 diode according to Claim 4 further comprising  
respective ohmic contacts to said substrate and said p-  
type aluminum gallium nitride layer.

6. A double heterostructure light emitting  
diode according to Claim 4 and further comprising an n-  
20 type gallium nitride epitaxial layer on said buffer  
layer, and wherein said n-type layer of aluminum  
gallium nitride in said heterostructure is on said n-  
type gallium nitride epitaxial layer.

7. A double heterostructure light emitting  
25 diode according to Claim 4 and further comprising a p-  
type layer of gallium nitride on said p-type layer of  
aluminum gallium nitride in said heterostructure; and  
an ohmic contact to said p-type layer of gallium  
nitride.

30 8. A double heterostructure light emitting  
diode according to Claim 4 wherein said substrate  
comprises conductive silicon carbide.

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9. A double heterostructure according to Claim 3 or Claim 4 wherein said n-type layer of aluminum gallium nitride has the formula  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  where  $1 > X > 0$ ; and said p-type layer of aluminum gallium nitride has the formula  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  where  $1 > X > 0$ .

10. A double heterostructure according to Claim 9 wherein X is about 0.1.

11. A double heterostructure light emitting diode according to Claim 4 wherein said gallium nitride layer is co-doped with both zinc and silicon.

12. A double heterostructure light emitting diode according to Claim 3 or Claim 4 wherein the n-type gallium nitride layer has a net doping density of between about  $1\text{E}18$  and  $4\text{E}18$ ; the p-type gallium nitride layer has a net doping density of about  $1\text{E}19$ ; and the n-type aluminum gallium nitride layer has a net doping density of about  $2\text{E}18$ .

13. A double heterostructure light emitting diode according to Claim 4 wherein said buffer layer comprises:

a first layer of gallium nitride and aluminum nitride; and

a second layer of gallium nitride and aluminum nitride adjacent to said first layer, and in which the mole percentage of aluminum nitride in said second layer is substantially different from the mole percentage of aluminum nitride in said first layer.

14. A double heterostructure light emitting diode according to Claim 4 wherein said buffer layer comprises a graded layer of aluminum gallium nitride

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that is substantially entirely aluminum nitride where it meets said substrate and then is progressively graded with increasing amounts of gallium until it is substantially entirely gallium nitride at its upper  
5 surface where it meets said double heterostructure.

15. A double heterostructure light emitting diode according to Claim 4 wherein said buffer layer comprises a conductive layer selected from the group consisting of gallium nitride, aluminum nitride, indium  
10 nitride, ternary Group III nitrides having the formula  $A_xB_{1-x}N$ , where A and B are Group III elements and where x is zero, one, or a fraction between zero and one, quaternary Group III nitrides having the formula  $A_xB_yC_{1-x-y}N$  where A, B, and C are Group III elements; x and y,  
15 are zero, one, or a fraction between zero and one, and 1 is greater than (x + y), and alloys of silicon carbide with such ternary and quaternary Group III nitrides.

16. A double heterostructure light emitting  
20 diode according to Claim 4 wherein said buffer layer comprises a first layer upon said substrate formed of a graded composition of silicon carbide aluminum gallium nitride in which the portion adjacent the substrate is substantially entirely silicon carbide and the portion  
25 furthest from the substrate is substantially entirely aluminum gallium nitride with the portions therebetween being progressively graded in content from predominantly silicon carbide to predominantly aluminum gallium nitride; and  
30 a second layer upon said first layer and formed of a graded composition of aluminum gallium nitride.



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17. A double heterostructure light emitting diode according to Claim 3 or Claim 4 wherein said gallium nitride active layer is compensated with a Group II acceptor selected from the group consisting of zinc, cadmium, magnesium, and a Group IV donor selected from the group consisting of silicon, germanium or carbon.

18. A double heterostructure light emitting diode according to Claim 4 wherein said buffer layer is insulating, and further comprising shorting contacts between said substrate and said double heterostructure.

19. A method of producing an active layer of compensated n-type gallium nitride for a double heterostructure light emitting diode that emits in the blue portion of the visible spectrum, the method comprising:

introducing vaporized sources of gallium, nitrogen, silicon and zinc into a chemical vapor deposition system that includes a semiconductor substrate compatible with the growth of gallium nitride thereon; and while

maintaining the temperature high enough to promote the epitaxial growth of zinc and silicon compensated gallium nitride, but lower than the temperature at which the gallium nitride would decompose.

20. A method according to Claim 19 wherein the temperature is maintained lower than the temperature at which the surface morphology of the epitaxial layer would become unacceptable for further epitaxial growth thereon.

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21. A method according to Claim 19 wherein the step of introducing a vaporized source of gallium comprises introducing trimethyl gallium; the step of introducing a vaporized source of nitrogen comprises  
5 introducing ammonia; the step of introducing a vaporized source of zinc comprises introducing diethyl zinc; and the step of introducing a vaporized source of silicon comprises introducing silane.

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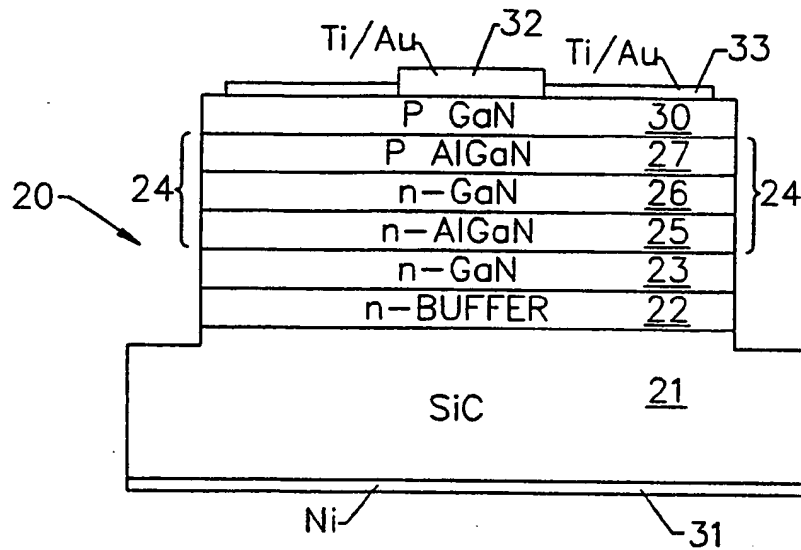


FIG. 1.

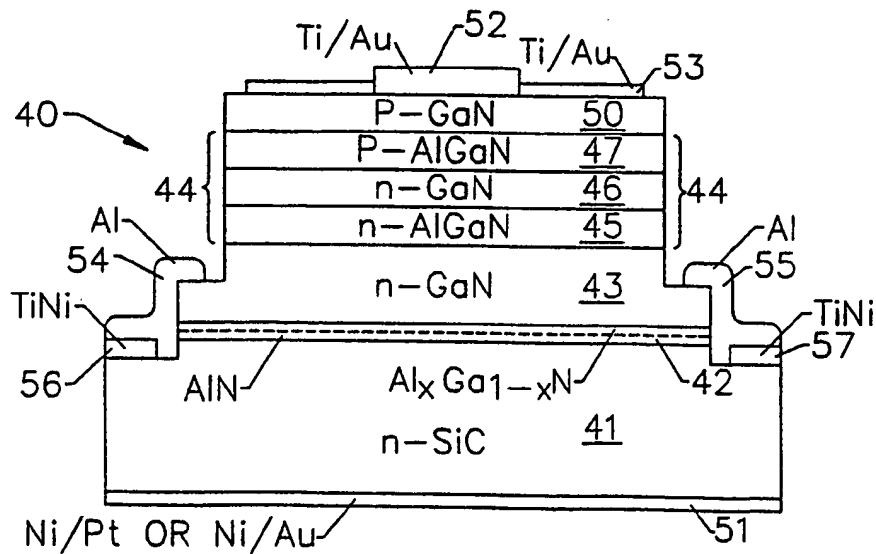


FIG. 2.

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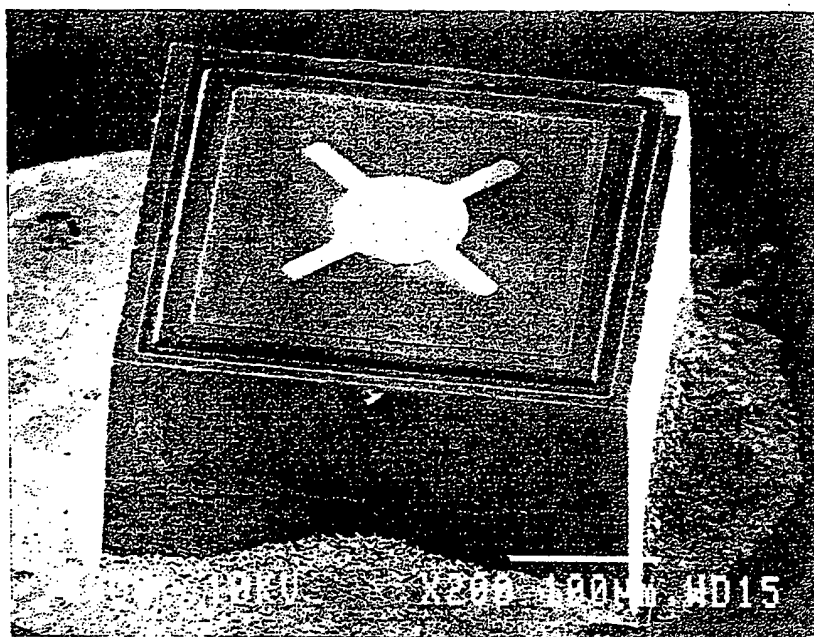
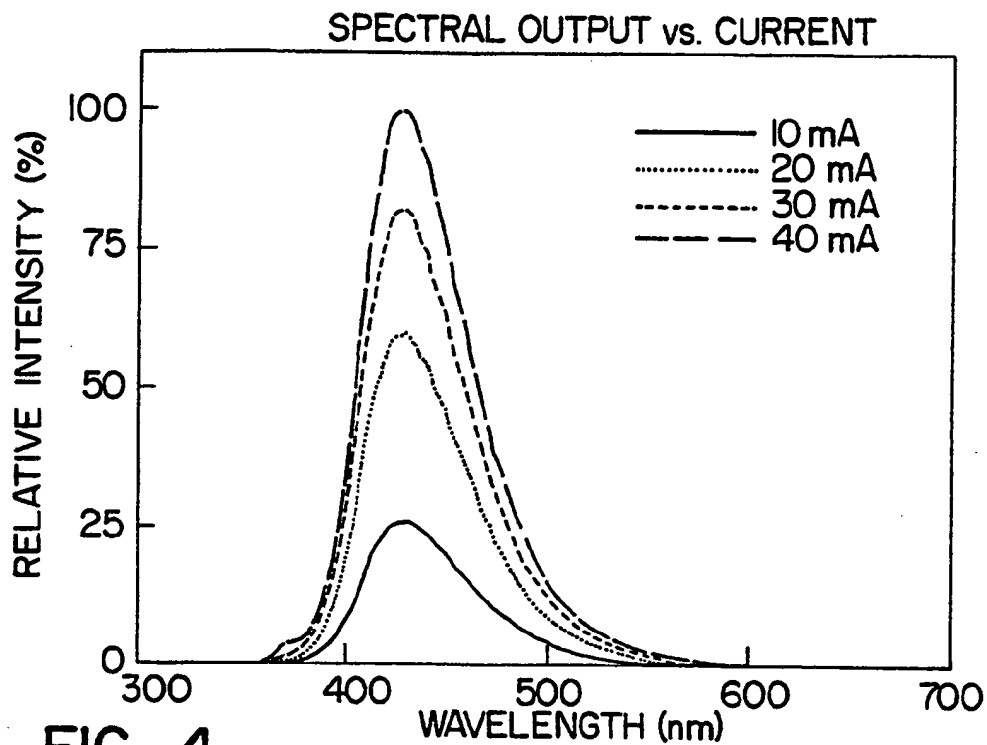
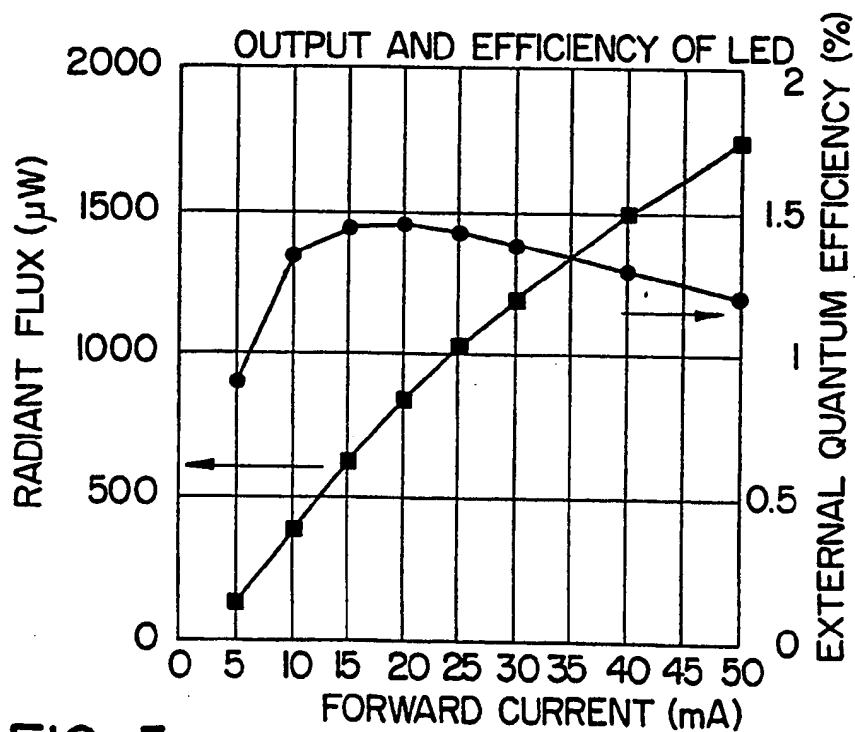
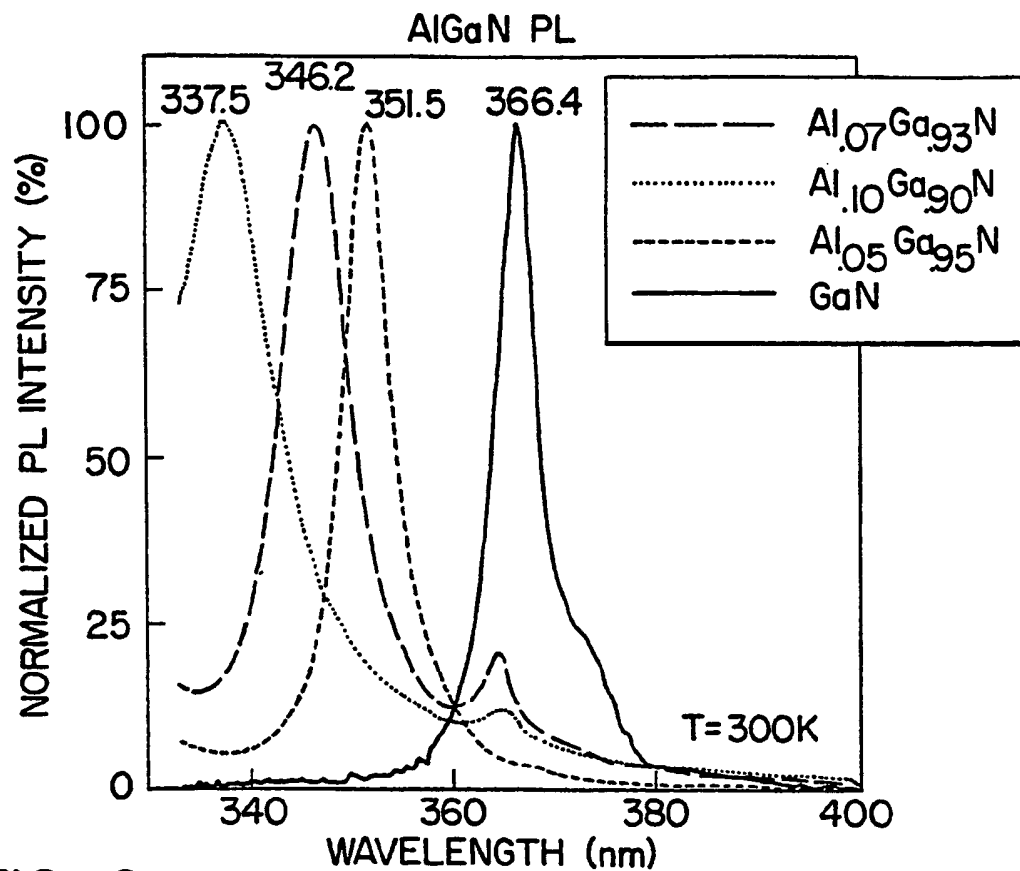
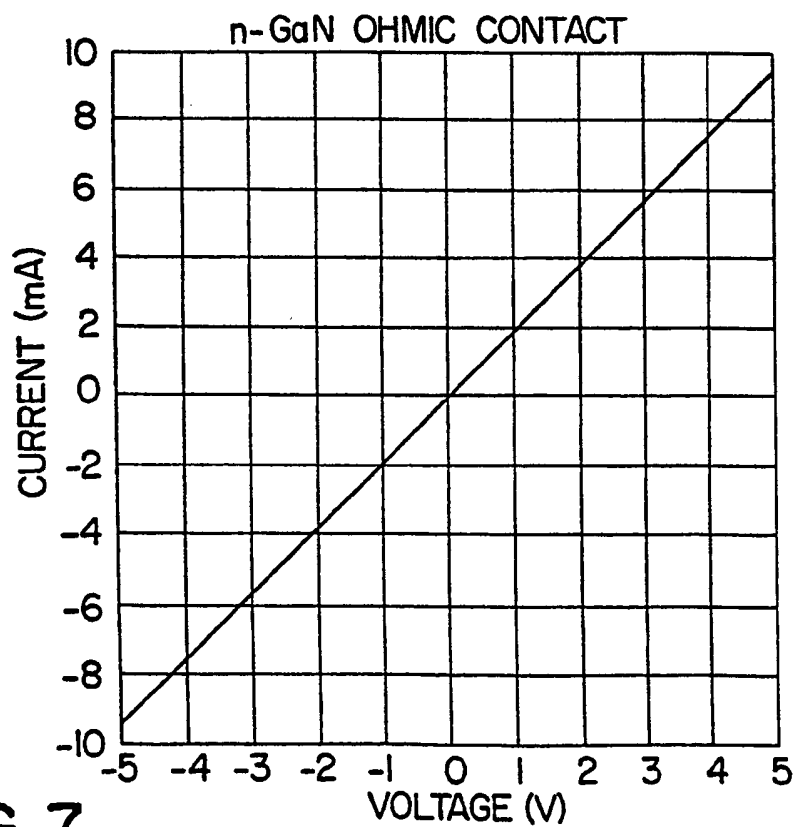


FIG. 3.

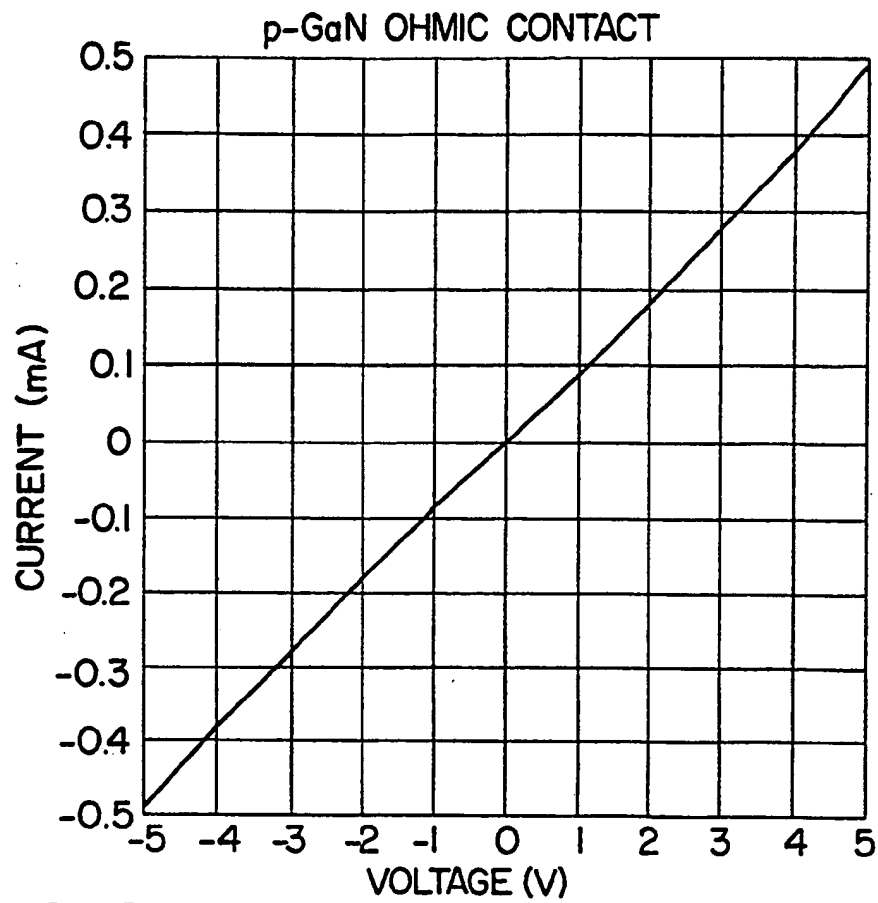
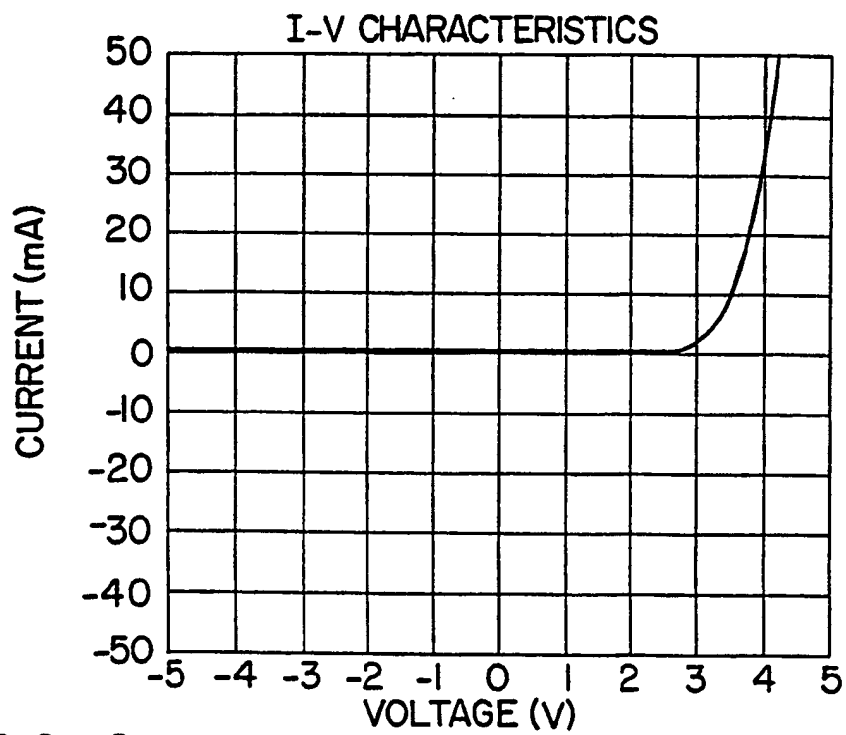
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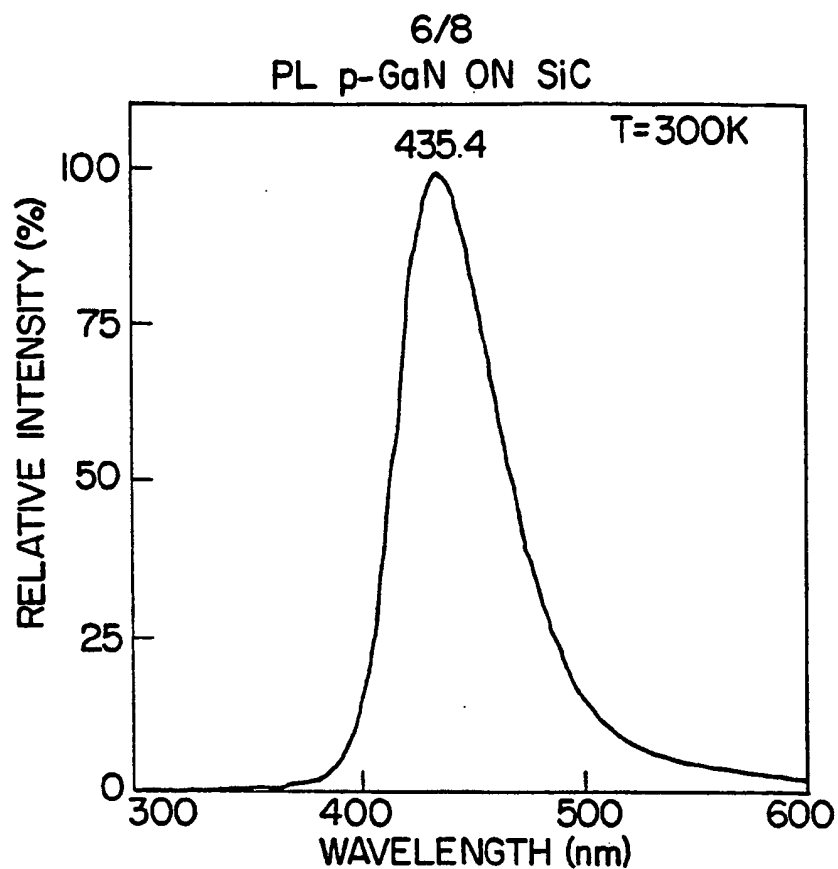
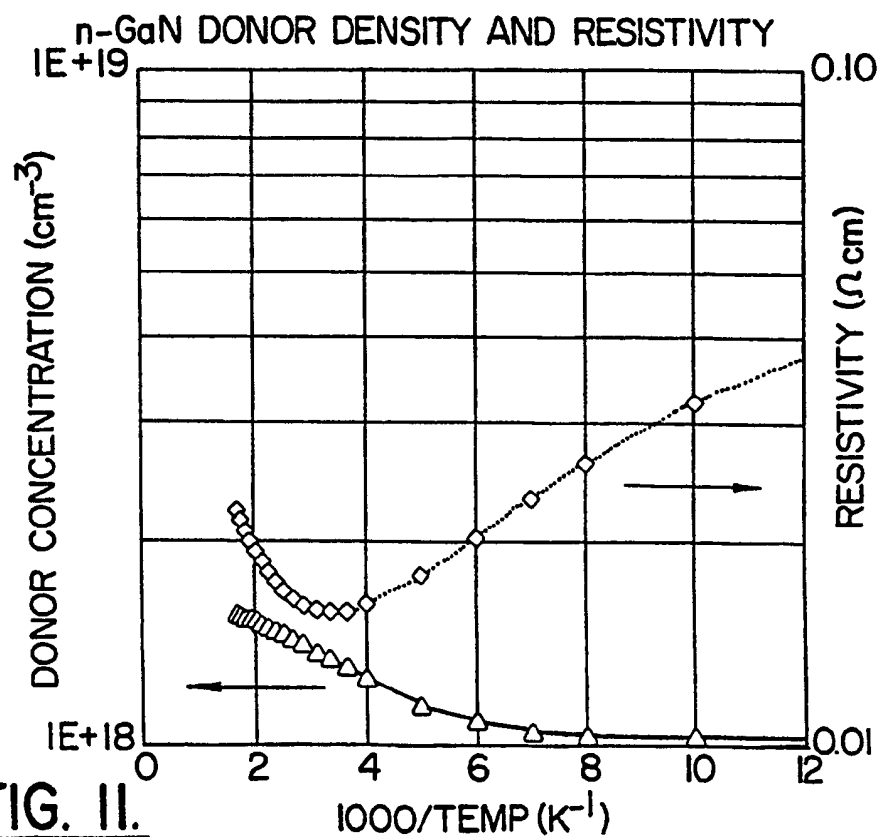
FIG. 4.FIG. 5.

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**FIG. 6.****FIG. 7.**

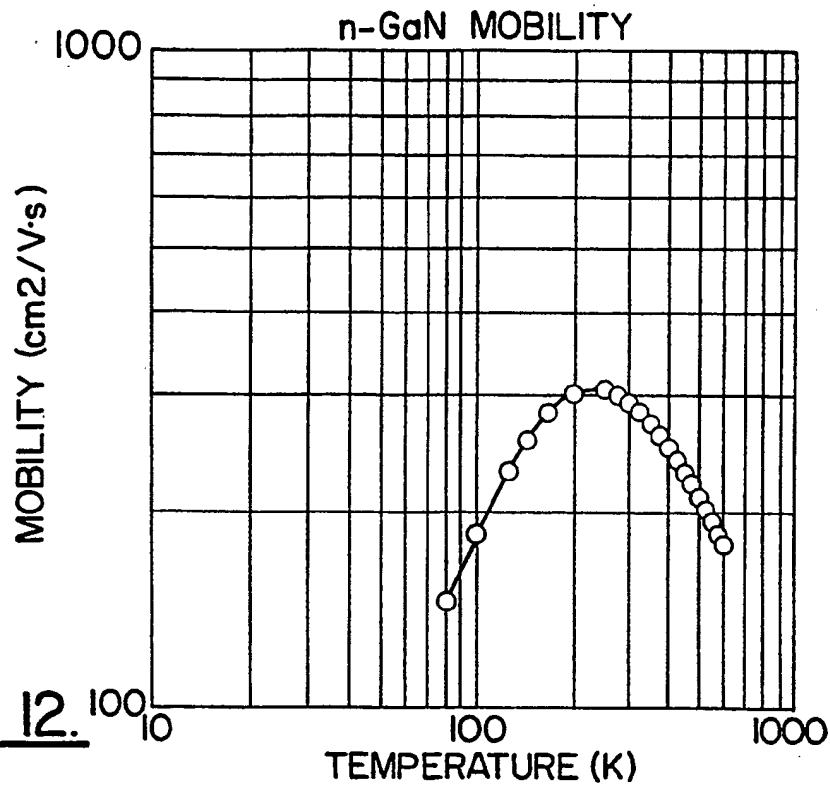
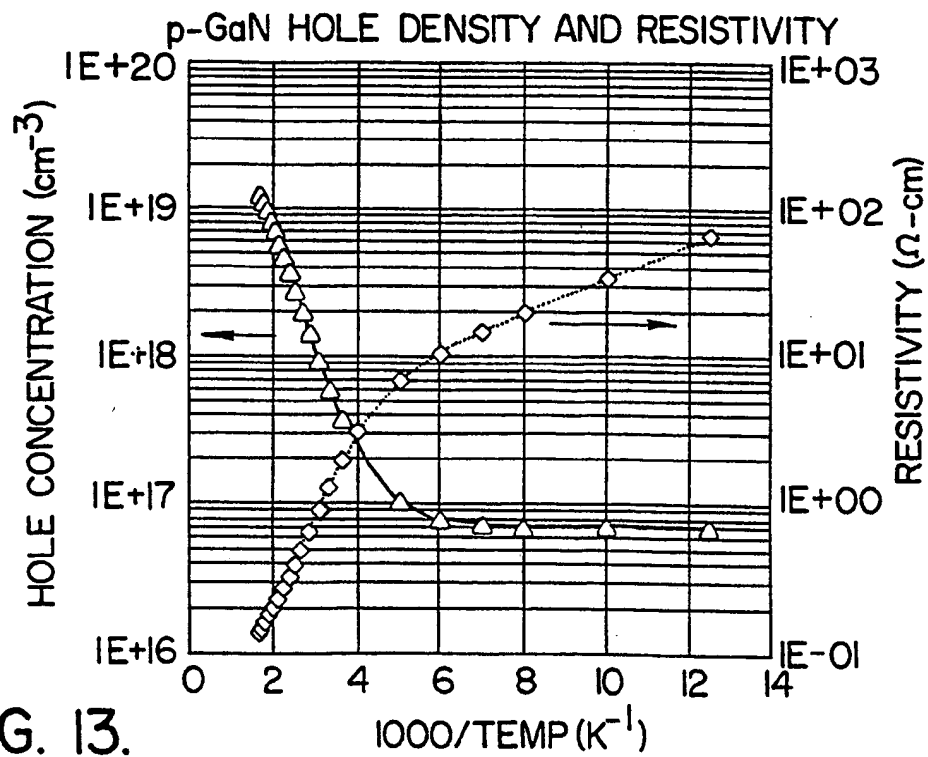
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FIG. 8.FIG. 9.

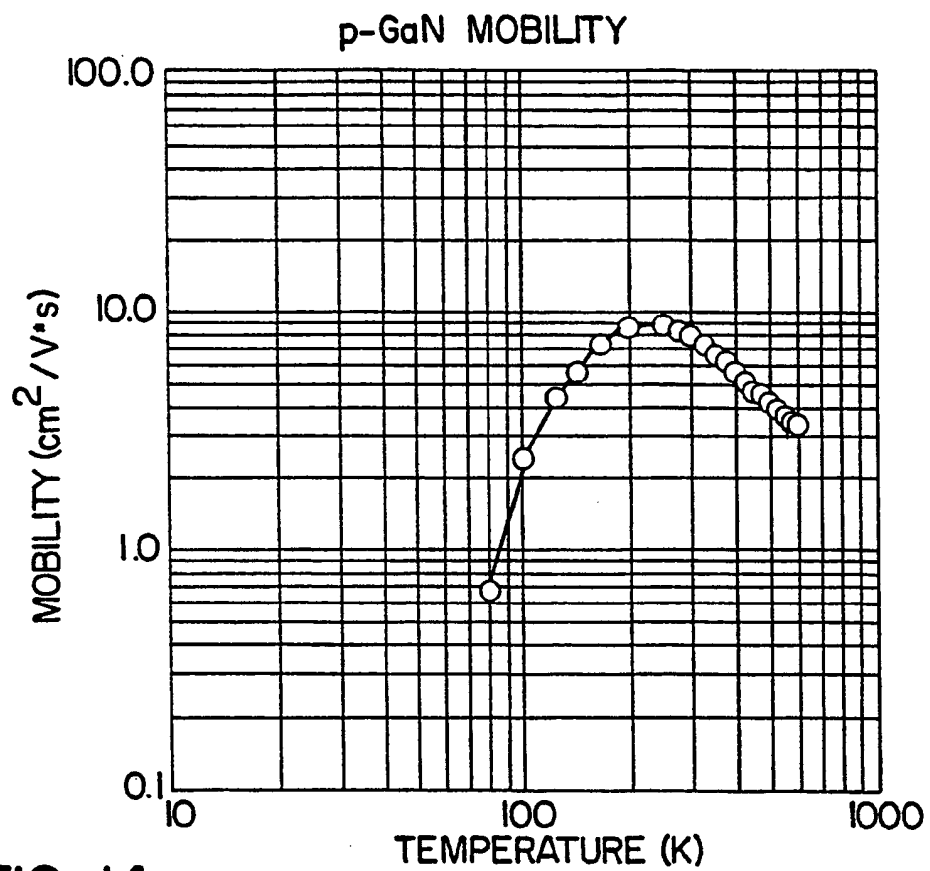
FIG. 10.FIG. II.



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FIG. 12.FIG. 13.

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**FIG. 14.**

## INTERNATIONAL SEARCH REPORT

Int: International Application No

PCT/US 96/05160

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 H01L33/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 95, no. 001 & JP,A,07 007182 (NICHIA CHEM IND LTD), 10 January 1995, see abstract	1-4,6,7, 9,11,17
Y	---	1-9,11, 13,17,18
Y	US,A,5 393 993 (EDMOND JOHN A ET AL) 28 February 1995 cited in the application see the whole document ---	1-9,11, 13,17,18
	--- -/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

16 August 1996

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International Application No

PCI/US 96/05160

## C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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P,Y	--- WO,A,96 09653 (CREE RESEARCH INC ;EDMOND JOHN ADAM (US); BULMAN GARY E (US); KONG) 28 March 1996 see claims	1-9,11, 16-21
A	--- OPTOELECTRONICS DEVICES AND TECHNOLOGIES, vol. 7, no. 1, 1 June 1992, pages 49-56, XP000294314 ISAMU AKASAKI ET AL: "PERSPECTIVE OF THE UV/BLE LIGHT EMITTING DEVICES BASED ON GAN AND RELATED COMPOUNDS" see page 54, paragraph 3.3	1,3,4,6, 9,10
A	--- EP,A,0 599 224 (NICHIA KAGAKU KOGYO KK) 1 June 1994  see column 9, line 21 - column 12, line 25; example 28  -----	1-4,6,7, 9-12,17, 19-21

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International Application No

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